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# THE SOLUBILITIES OF COMPRESSED ACETYLENE GAS IN LIQUIDS, II

## The Solubility of Compressed Acetylene Gas in Methanol\*

BY RYO KIYAMA AND HIROYUKI HIRAOKA

### Introduction

It was reported<sup>1)</sup> previously that the solubility of compressed acetylene gas in water is nearly proportional to the fugacity of acetylene at pressures up to 5 kg/cm<sup>2</sup>, 15 kg/cm<sup>2</sup>, 35 kg/cm<sup>2</sup> and 40 kg/cm<sup>2</sup> at 1°C, 10°C, 20°C and 30°C respectively and at low temperatures the measurement of the solubility under higher pressures is impossible to be performed because acetylene hydrate is produced. However, it would be a special case for the solubility to be proportional to the fugacity of the solute.

Hildebrand and Scott<sup>2)</sup> have developed the theory of the solubility of nonpolar gases in nonpolar solvents and Gjaldbaek and Andersen<sup>3)</sup> gave the consideration upon the solubility in polar solvents. It is of interest theoretically and practically to know how the solubilities of acetylene in other polar and nonpolar solvents change with the pressure or the fugacity of acetylene. There are several methods of the approximate calculation of the fugacity of the dissolved gas in the solvent with high vapor pressure. For examples, we may calculate the fugacity from the relation (1), with a knowledge of the concentration of the solvent in the gaseous phase in equilibrium with the liquid phase (cf. 2) p. 238),

$$\ln f_2 = \ln N_2 f_2^0 + \frac{P\Delta}{RT} N_1^2, \quad (1)$$

where  $N_1$  and  $N_2$  are the mole fractions of the solvent and the solute in the gaseous phase respectively at the temperature  $T$  and at the pressure  $P$ ,  $f_2$  the fugacity of the solute in the gaseous and liquid phases, both of which are in equilibrium and  $f_2^0$  that of the pure solute,  $\Delta$  the difference between the second virial coefficient of the mixture and the sum of the coefficients of the pure components. Or, we may calculate the fugacity from

\* This investigation has been done by H. Hiraoka, being in the postgraduate course, under the direction of Prof. R. Kiyama.

1) H. Hiraoka, *This Journal*, 24, 13 (1954)

2) J. H. Hildebrand and Scott, *Solubility of Nonelectrolytes*, Reinhold Publishing Co., New York (1950)

3) J. Chr. Gjaldbaek and Erik Krogh Andersen, *Acta Chem. Scand.*, 8, 1398 (1954)

the thermodynamic relation (2), with a knowledge of the change of the partial molal volume of the solute in the liquid phase with pressure,

$$\ln \frac{f_2}{f_2^*} = \frac{1}{RT} \int_{p^*}^p \bar{V}_2 dP, \quad (2)$$

where  $\bar{V}_2$  is the partial molal volume of the solute in the liquid phase.

In this paper the results of the measurements of the solubility of compressed acetylene gas in methanol are given and the relation between the fugacity and the solubility will be given in the later paper.

The solubility of compressed acetylene gas in methanol, as given in later, follows Henry's law at low pressures but at higher pressures the solubility becomes larger than that expected from the law, as in the case of the dissolution of compressed acetylene gas in acetone<sup>4)</sup>.

In the method of the measurement which we are adopting for the solubility of compressed gas in liquid, it is necessary to know the solubility at one atmospheric pressure. In this paper the solubility of acetylene in methanol at one atmospheric pressure, which has never been reported until now, is given.

### Experimentals

**Materials** Acetylene gas is prepared from calcium carbide and water and is purified through refining reagents. The purity of acetylene gas used is 99.5 ~ 99.6%. Methanol used as the solvent is fractionated between 64.7° and 64.8°C at 1 atm and its density,  $S_{15/15} = 0.79952$ , which corresponds to the purity of 98.91%<sup>5)</sup>.

#### Apparatus and Experimental procedures

*At the atmospheric pressure* The apparatus is one of the Ostwald types and consists of a gas burette graduated at every 0.1 cc and an absorption pipette of about 15 cc capacity. The measurement proceeds as follows. The absorption pipette is evacuated by means of an aspirator and a small quantity of methanol is allowed into the pipette to replace the air by the methanol vapor. After the complete replacement, the pipette is filled with 4 ~ 7 cc of methanol and then mercury with caution not to admit the air into the pipette. Waiting for temperature equilibrium for a while, the mercury in the pipette is expelled, while the acetylene gas is allowed into the pipette from the gas burette. The volume of methanol is determined from the difference between the volume of the pipette and that of the mercury contained in the pipette before its ejection. The pipette is shaken by hand until no absorption takes place. The volume of the gas absorbed is determined from the difference between the initial reading and the final one on the gas burette. The dissolved air in methanol is removed by boiling.

*Under pressure* The apparatus and the procedure are the same as those described

4) P. Hölemann and R. Hasselmann, *Chem. Ing. Tech.*, **25**, 466 (1953)

5) Landolt-Börnstein, *Physikalisch-Chemische Tabellen* (5 auflage) **1**, p. 453

in the previous paper with the exception that the liquid burette is graduated at every 0.01 cc, the capacity of graduated part being 5 cc.

### Results

The vapor pressure and density of pure methanol at each temperature necessary for the calculation of the solubility, are taken from the measurements of Ramsay *et al.*<sup>6)</sup> and those of Klason *et al.*<sup>7)</sup>, respectively. The solubility at one atmospheric pressure is given in Table 1 by mole fraction ( $N$ ) of acetylene and Bunsen's coefficient ( $\phi$ ), which is the

Table 1 The solubilities of acetylene in methanol at one atmospheric pressure

Temp., C°	0	5	10	15	20
Solubility					
Bunseen's coff.	20.0	17.0	14.8	12.9	11.3
Mole fraction	0.0340	0.0294	0.0258	0.0227	0.0201

volume (cc) of the gas reduced to 0°C and 1 atm that is absorbed by 1 cc of the solvent under one atmospheric partial pressure of the solute gas. The mole fraction of acetylene could be calculated from the formula (3) with less deviation than 1%,

$$\log_{10} N = \frac{9.206}{T} \times 10^2 - 4.8403, \quad (3)$$

where  $T$  is the absolute temperature.

As acetylene has somewhat large solubility in methanol at the atmospheric pressure, the coefficient of dilatation by absorption  $\delta$ , which is the ratio of the volume increment of the solvent to the quantity of the absorbed gas, should be taken into account in the calculation of the solubility. Then the solubility  $\gamma$  which is the number of cc of acetylene (S. T. P.) contained in 1 cc of methanol at each experimental temperature is calculated from the formula (4) (*cf.* 1)), in whose derivation it is assumed that the acetylene gas at

Table 2 The solubilities of acetylene in methanol  
(cc-C<sub>2</sub>H<sub>2</sub>/cc-Methanol)

Temperatures °C	0	10	20	30
Total pressures, kg/cm <sup>2</sup>				
5	86.3	66.4	52.1	37.1
10	185.8	131.7	98.9	79.7
15	340.9	210.7	157.1	120.7
20	734.2	322.4	228.4	168.0
25		550.2	334.2	224.7
30			509.6	319.6

6) Landolt-Börnstein, *Physikalisch-Chemische Tabellen* (5 auflage) 2, p. 1361

7) *ibid.*, 1, p. 452

one atmospheric pressure follows the law of ideal gas and a mixture of acetylene and the methanol vapor at the same pressure does Dalton's law,

$$\gamma = \frac{d^r}{d^T} \cdot \frac{P-b}{760} \cdot \left( V \cdot \frac{273.1}{T'} + \frac{\phi}{1 + \phi \cdot \delta \cdot (P-b)/760} \right) / \left( 1 - \phi \cdot \frac{P-b}{760} \cdot \delta \right), \quad (4)$$

where  $d_T$  and  $d_{T'}$  denote the densities of methanol at the temperature  $T$  in the apparatus of the high pressure equilibrium and at the temperature  $T'$  in the burettes, respectively;  $b$  the vapor pressure of methanol at the temperature  $T'$  and  $V$  the volume (cc) of the gas separated from the liquid in the burettes at the temperature  $T'$  and at the barometric pressure  $P$ . The Bunsen's coefficient  $\phi$  at the temperature  $T'$  is calculated using the formula (3). Horiuti<sup>8)</sup> measured the coefficients of dilatation by absorption of acetylene in several liquids but not in methanol. According to the results of his measurements the values of  $\delta$  of acetylene are smaller in the solvents of larger solubility in approximate manner and for carbon tetrachloride, chlorobenzene, acetone and methylacetate,  $2.340 \times 10^{-3}$ ,  $2.150 \times 10^{-3}$ ,  $2.195 \times 10^{-3}$ ,  $2.108 \times 10^{-3}$ , and  $2.108 \times 10^{-3}$  respectively. In methanol acetylene gas has larger solubility than that in benzene and chlorobenzene but smaller than that in acetone and methylacetate. Then in our calculation  $2.15 \times 10^{-3}$  is used as the value of  $\delta$ , and the use of this value would be allowed because the value of  $\delta$  contributes only slightly to the value of the large solubility and the difference among the values of  $\delta$  of acetylene in various solvents is comparatively small. In Tables 2 and 3 the solubility  $\gamma$  and the mole fraction  $N$  are given. In Fig. 1 the solubilities  $\gamma$  are plotted against the total pressures and in Fig. 2 the logarithms of the mole fraction  $N$  are plotted against the reciprocal of the absolute temperatures. As will be seen from Fig. 1, the solubility is nearly proportional to the total pressure at low pressures but it deviates considerably from Henry's law at higher pressures and this deviation is larger at low temperature. In Fig. 2 the linear relations between  $\log N$  and  $T^{-1}$  are obtained up to about  $10 \text{ kg/cm}^2$  but at the higher pressure the curves deviate from the linearity in the range of these experimental temperatures.

Table 3 The solubilities of acetylene in methanol  
(Mole fraction  $N$ )

Temperatures °C Total pressures, kg/cm <sup>2</sup>	0	10	20	30
5	0.132	0.106	0.0860	0.0635
10	0.2470	0.1905	0.152	0.127
15	0.3757	0.2734	0.2211	0.1807
20	0.5646	0.3654	0.2920	0.2349
25		0.4957	0.3764	0.2911
30			0.4793	0.3687

8) J. Horiuti, *Sci. Papers Inst. Phys. Chem. Research, Tokyo*, **17**, 125 (1931)

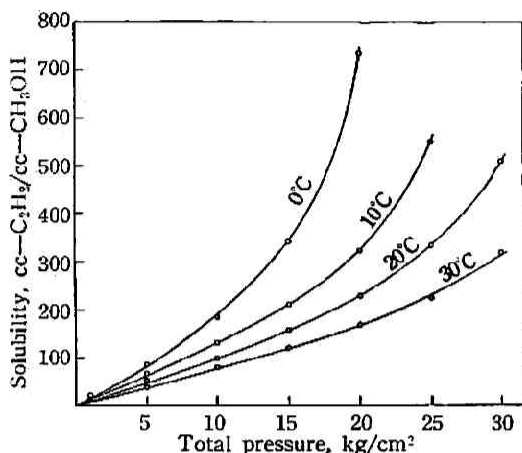


Fig. 1 The solubilities of acetylene in methanol against total pressure

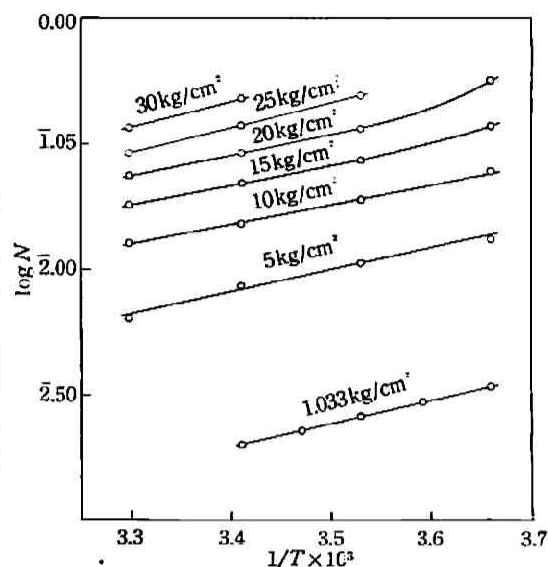


Fig. 2 The relations between mole fraction and temperature

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